Exactly realizable bounds on the trapping constant and permeability of porous media

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(Received 14 July 2004; accepted 15 October 2004; published online 15 December 2004)

Sandstone, granular media, bone, wood, and cell membranes are just a few examples of porous media that abound in Nature and in synthetic situations. Two important effective properties of fluid-saturated porous media that have been extensively studied are the trapping constant γ and scalar fluid permeability k. Exact expressions for the "void" bounds on γ and k for coated-spheres and coated-cylinders models of porous media are derived. In certain instances, the bounds are shown to be optimal, i.e., the void bounds coincide with the corresponding exact solutions of γ and k for these coated-inclusions models. In the optimal cases, we obtain exact expressions for the relevant length scale that arises in the void bounds, which depends on a two-point correlation function that characterizes the porous medium. By contrast, optimal bounds on the effective conductivity and elastic moduli of composite media have long been known. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1829379]

I. INTRODUCTION

It is well established that the effective properties of a random heterogeneous material depend on an infinite set of statistical correlations that characterize the microstructure.[1] Thus, exact determinations of effective properties are available for only a few special cases.[1–3] In the absence of exact solutions, one can estimate the effective properties using approximation schemes[1,2,4] or by deriving rigorous bounds on them.[1–3,5–8] Bounds are useful because: (i) As successively more microstructural information is included, the bounds become progressively narrower; (ii) one of the bounds can provide a relatively sharp estimate of the property for a wide range of conditions, even when the reciprocal bound diverges from it; and (iii) they can be utilized to test the merits of a theory or computer experiment.[1] Moreover, it is highly desirable to find optimal bounds when possible and the microstructures that attain them.

Perhaps the best known bounds in the cases of the effective conductivity and effective bulk modulus of two-phase media are the Hashin–Shtrikman bounds.[5,6] These are optimal bounds, given the phase volume fractions, because they are realizable by, among other geometries,[1–3] certain coated-spheres and coated-cylinders assemblages in three and two dimensions, respectively. The coated-spheres model has been extended to the effective conductivity of multiphase composites.[9–11]

Sandstone, granular media, bone, wood, and cell membranes are just a few examples of porous media that abound in Nature and in synthetic situations. The trapping constant γ[1,12–14] and scalar fluid permeability k[1,4,12,15–19] are two important effective properties of fluid-saturated porous media. Bounds on the trapping constant[1,20–24] and fluid permeability[1,25–28] of porous media have been derived and computed. Heretofore, however, microstructures that exactly realize (or attain) any of these bounds have yet to be identified. Torquato[1] observed that the difficulty in identifying optimal microstructures for these classes of problems lies in the fact that γ and k are length-scale dependent quantities and known bounds on them depend nontrivially on the specific forms of two-point and higher-order correlation functions. For example, the so-called *void* bounds on γ and k (Refs. 1, 24, and 28) depend on the probability $S_2(r)$ of finding two points—separated by a distance r—both in the pore phase of an isotropic porous medium and have been evaluated for various particle models for the trapping constant[1,24,29] and fluid permeability.[1,25,26,28]

In this article, we derive analytical expressions for the *void* bounds on the trapping constant γ and fluid permeability k for the coated-spheres and coated-cylinders models of porous media. We demonstrate that in some instances the void bounds are optimal, i.e., the void bounds coincide with the corresponding exact solutions of γ and k for these particular coated-inclusions porous-media models. In these cases, we obtain exact expressions for the relevant length scale that arises in the void bounds, which depends on a two-point correlation function that characterizes the porous medium. In a recent letter,[30] we reported some of these results but very few details concerning the derivation of the bounds were presented. The purpose of this article is to provide detailed derivations of the exact expressions of γ and k for the coated-sphere and coated-cylinder models of porous media, and to display the bounds graphically.

Section II briefly summarizes the basic equations and variational void bounds for the trapping and flow problems. In Sec. III, we derive some exact results involving the Green's function of the Laplace operator for the coated-spheres and coated-cylinders models. We derive our major results for the trapping constant and fluid permeability in Secs. IV–VI. In Sec. VII, we present our conclusions and discuss future work.

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II. BASIC EQUATIONS AND VARIATIONAL BOUNDS

Each realization of the porous medium occupies the region of space $\mathcal{V} \in \Re^d$ of volume V that is partitioned into two disjoint regions: A pore space (phase) $\mathcal{V}_P$ of porosity ϕ_P and a solid space (phase) $\mathcal{V}_S$ of volume fraction $\phi_S = 1 - \phi_P$. Clearly, $\mathcal{V}_P \cup \mathcal{V}_S = \mathcal{V}$ and $\mathcal{V}_P \cap \mathcal{V}_S = \emptyset$. Let $\partial\mathcal{V}$ denote the surface of interface between $\mathcal{V}_P$ and $\mathcal{V}_S$. The pore-space *indicator function* $\mathcal{I}^{(P)}(\mathbf{x})$ is given for $\mathbf{x} \in \mathcal{V}$ by

$$\mathcal{I}^{(P)}(\mathbf{x}) = \begin{cases} 1, & \mathbf{x} \text{ in } \mathcal{V}_P \\ 0, & \text{otherwise}. \end{cases} \tag{1}$$

The indicator function $\mathcal{M}(\mathbf{x})$ for the interface is defined as

$$\mathcal{M}(\mathbf{x}) = |\nabla \mathcal{I}^{(P)}(\mathbf{x})|. \tag{2}$$

For statistically homogeneous media, the ensemble averages of the indicator functions (1) and (2) are, respectively, equal to the phase volume fraction ϕ_P , i.e.,

$$\phi_P = \langle \mathcal{I}^{(P)}(\mathbf{x}) \rangle, \tag{3}$$

and the specific surface s (interfacial area per unit volume), i.e.,

$$s = \langle \mathcal{M}(\mathbf{x}) \rangle, \tag{4}$$

where angular brackets denote an ensemble average.

A. Trapping problem

Consider the steady-state trapping problem.[1] The pore space $\mathcal{V}_P$ is the region in which diffusion occurs (i.e., trap-free region), and $\mathcal{V}_S$ is the trap region. The concentration field of the reactants $c(\mathbf{x})$ at position $\mathbf{x}$ exterior to the traps is governed by the mass conservation equation

$$D\nabla^2 c(\mathbf{x}) + G = 0 \quad \text{in} \quad \mathcal{V}_P, \tag{5}$$

with the boundary condition at the pore–trap interface, for the case of perfectly absorbing traps, given by

$$c(\mathbf{x}) = 0 \quad \text{on} \quad \partial\mathcal{V}. \tag{6}$$

Here, D is the diffusion coefficient of the reactant, G is a generation rate per unit trap-free volume. The two-scale homogenization theory enables one to show that the trapping constant γ obeys the first-order rate equation

$$G = \gamma D C, \tag{7}$$

where C represents an average concentration field. For a statistically homogeneous and ergodic medium, it can be demonstrated that the trapping constant has the alternative representation[1,23]

$$\gamma^{-1} = \langle u \rangle = \lim_{V\to\infty} \frac{1}{V}\int_{\mathcal{V}} u(\mathbf{x}) d\mathbf{x}, \tag{8}$$

where $u(\mathbf{x})$ is the scaled concentration field that solves the boundary-value problem

$$\nabla^2 u(\mathbf{x}) = -1, \quad \mathbf{x} \in \mathcal{V}_P, \tag{9}$$

$$u(\mathbf{x}) = 0, \quad \mathbf{x} \in \partial\mathcal{V}. \tag{10}$$

It follows that the trapping constant γ for any d has dimensions of the inverse of length squared.[1]

A variational principle was formulated by Rubinstein and Torquato[23] in terms of a trial function $\nu(\mathbf{x})$, which enables one to obtain the following lower bound on γ for ergodic media:

$$\gamma \geq \frac{1}{\langle \nabla v(\mathbf{x}) \cdot \nabla v(\mathbf{x}) \mathcal{I}^{(P)}(\mathbf{x}) \rangle}, \tag{11}$$

where $v(\mathbf{x})$ is required to satisfy the Poisson equation

$$\nabla^2 v(\mathbf{x}) = -1, \; \mathbf{x} \in \mathcal{V}_P. \tag{12}$$

Elsewhere, Torquato and Rubinstein[24] constructed what they referred to as the *void* lower bound in three dimensions by using a specific trial field. The generalization of this trial field to any dimension $d \geq 2$ is given by[1]

$$v(\mathbf{x}) = \frac{1}{\phi_S}\int_{\mathcal{V}} g(\mathbf{x}-\mathbf{y})[\mathcal{I}^{(P)}(\mathbf{y}) - \phi_P] d\mathbf{y}, \tag{13}$$

where

$$g(\mathbf{r}) = \begin{cases} \dfrac{1}{2\pi}\ln\left(\dfrac{1}{r}\right), & d = 2 \\ \dfrac{1}{(d-2)\Omega(d)}\dfrac{1}{r^{d-2}}, & d \geq 3, \end{cases} \tag{14}$$

is the d-dimensional Green's function for the Laplace operator, $\Omega(d)$ is the total solid angle contained in a d-dimensional sphere given by

$$\Omega(d) = \frac{2\pi^{d/2}}{\Gamma(d/2)}, \tag{15}$$

ϕ_S is volume fraction of the trap phase, and $r \equiv |\mathbf{r}|$. Substitution of trial field (13) into the variational principle (11) yields the void lower bound on γ for general statistically homogeneous and isotropic d-dimensional porous media[1] as

$$\gamma \geq \frac{\phi_S^2}{\ell_P^2}, \tag{16}$$

where ℓ_P is a pore length scale defined by

$$\ell_P^2 = \begin{cases} -\displaystyle\int_0^\infty [S_2(r) - \phi_P^2] r \ln r dr, & d = 2 \\ \dfrac{1}{(d-2)}\displaystyle\int_0^\infty [S_2(r) - \phi_P^2] r dr, & d \geq 3, \end{cases} \tag{17}$$

and $S_2(\mathbf{r})$ is the two-point correlation function defined by

$$S_2(\mathbf{r}) = \langle \mathcal{I}^{(\mathcal{P})}(\mathbf{x}) \mathcal{I}^{(\mathcal{P})}(\mathbf{x}+\mathbf{r}) \rangle. \tag{18}$$

The function $S_2(\mathbf{r})$ can also be interpreted as being the probability of finding two points separated by the displacement vector $\mathbf{r}$ in the pore space.[1]

B. Flow problem

Using homogenization theory, Rubinstein and Torquato[28] derived the conditions under which the slow flow of an incompressible viscous fluid through macroscopically anisotropic random porous medium is described by Darcy's law

$$\mathbf{U} = -\frac{1}{\mu}\mathbf{k}\cdot\nabla p_0, \tag{19}$$

where $\mathbf{U}$ is the average fluid velocity, ∇p_0 is the applied pressure gradient, μ is the dynamic viscosity, and $\mathbf{k}$ is the symmetric fluid permeability tensor. In particular, for the special case of macroscopically isotropic media, the scalar fluid permeability $k=\mathrm{Tr}(\mathbf{k})/d$ (where Tr denotes the trace operation) is given by

$$k = \langle \mathbf{w}\cdot\mathbf{e}\rangle = \lim_{V\to\infty}\frac{1}{V}\int_{\mathcal{V}}\mathbf{w}(\mathbf{x})d\mathbf{x}, \tag{20}$$

where $\mathbf{w}$ is a scaled velocity and Π is a scaled pressure, which satisfy the scaled Stokes equations

$$\nabla^2\mathbf{w} = \nabla\Pi - \mathbf{e} \quad \text{in} \quad \mathcal{V}_P, \tag{21}$$

$$\nabla\cdot\mathbf{w} = 0 \quad \text{in} \quad \mathcal{V}_P, \tag{22}$$

$$\mathbf{w} = 0 \quad \text{on} \quad \partial\mathcal{V}, \tag{23}$$

and $\mathbf{e}$ is a unit vector. It follows that the permeability k for any d has dimensions of length squared.[1]

A "void" upper bound on the permeability was derived by Prager[25] using a variational principle. Afterward, Berryman and Milton[26] corrected a normalization constraint in the Prager variational principle using a volume-average approach and thus corrected a constant factor in the void bound. Rubinstein and Torquato[28] developed upper and lower bound variational principles utilizing an ensemble-average approach and also derived the void upper bound.

For our purposes, the Rubinstein–Torquato variational principle for the upper bound on the permeability is the most natural starting point. This variational principle states that for ergodic media the trial function $\mathbf{q}(\mathbf{x})$ enables one to obtain the following upper bound on k:

$$k \geqslant \langle \mathbf{q}(\mathbf{x}) : \nabla\mathbf{q}(\mathbf{x})\mathcal{I}^{(P)}(\mathbf{x})\rangle, \tag{24}$$

where $\mathbf{q}(\mathbf{x})$ is required to satisfy the momentum equation

$$\nabla\times\nabla^2(\mathbf{q}+\mathbf{e}) = \mathbf{0}, \quad \mathbf{x}\in\mathcal{V}_P. \tag{25}$$

Rubinstein and Torquato[28] constructed the *void* upper bound on k in three dimensions by using a specific trial field. The generalization of this trial field to any space dimension $d \geqslant 3$[1] is given by

$$\mathbf{q}(\mathbf{x}) = \frac{1}{\phi_S}\int_{\mathcal{V}}\mathbf{\Psi}(\mathbf{x}-\mathbf{y})\cdot\mathbf{e}[\mathcal{I}^{(P)}(\mathbf{y})-\phi_P]d\mathbf{y}, \tag{26}$$

where

$$\mathbf{\Psi}(\mathbf{r}) = \frac{d}{(d^2-3)\Omega(d)r^{d-2}}[\mathbf{I}+\mathbf{nn}], \quad d\geqslant 3, \tag{27}$$

is the d-dimensional Green's function Ψ (second-order tensor) associated with the velocity for Stokes flow, $\mathbf{n}=\mathbf{r}/r$, and ϕ_S is the volume fraction of the obstacles. Substitution of trial field (26) into the variational principle (24) yields the void upper bound on k for general statistically homogeneous and isotropic d-dimensional porous media[1] as

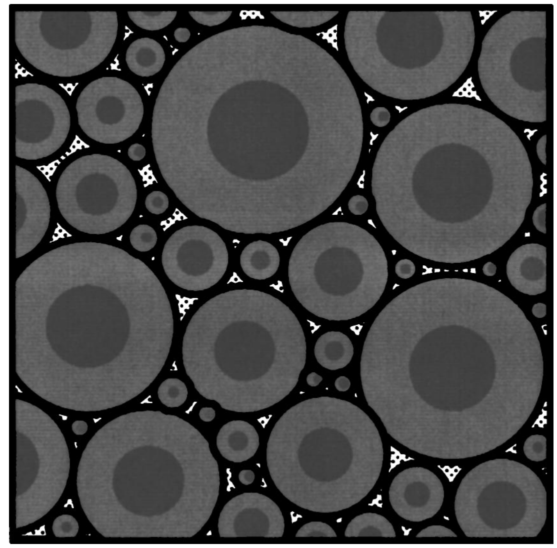

FIG. 1. Schematic of the coated-spheres model microstructure.

$$k \leqslant \frac{(d+1)(d-2)}{d^2-3}\frac{\ell_P^2}{\phi_S^2}, \quad d\geqslant 3, \tag{28}$$

where ℓ_P is the length scale defined by Eq. (17), which is precisely the same as the one that arises in the void lower bound on the trapping constant γ for $d\geqslant 3$.[31,13,1]

III. COATED-SPHERES MODEL

The coated-spheres model[5] consists of composite spheres that are composed of a spherical core of phase 2 (inclusion) and radius R_I, surrounded by a concentric shell of phase 1 (matrix) and outer radius R_M. The ratio $(R_I/R_M)^d$ is fixed and equal to the inclusion volume fraction ϕ_2 in space dimension d. The composite spheres fill all space, implying that there is a distribution in their sizes ranging to the infinitesimally small (see Fig. 1). The inclusion phase is always disconnected and the matrix phase is always connected (except at the trivial point $\phi_2=1$).

A. Size-distribution restrictions

The coated-spheres model places restrictions on the size distribution of the composite spheres. Consider a macroscopically large but finite-sized spherical sample of the porous medium of volume V and radius $\mathcal{R}$ in d dimensions. The coated-spheres porous medium occupies the space $\mathcal{V}$ and is partitioned into two disjoint regions: A matrix phase $\mathcal{V}_1$ and inclusion phase $\mathcal{V}_2$. The composite spheres are uniformly distributed in $\mathcal{V}$ and the corresponding radius of the inclusion. It is clear that the radius of the largest composite sphere, which we denote by $R_{\max}$, must be such that it obeys the condition $R_{\max} \ll \mathcal{R}$. Thus, the specimen is virtually statistically homogeneous. Ultimately, we will take the infinite-volume limit, i.e., $\mathcal{R}\to\infty$ or $V\to\infty$. Without loss of generality, we will assume that the composite spheres possess an infinite number of discrete sizes. Let ρ_k be the number density (number of particles per unit volume) of the kth type of composite sphere of radius R_{M_k} and let R_{I_k} denote the corresponding radius of the inclusion. Moreover, we know that the fraction of space covered by the composite spheres, denoted by Φ, is unity, and therefore we have the following condition on the size distribution:

$$\Phi = \sum_{k=1}^{\infty} \rho_k v_1(R_{M_k}) = 1, \tag{29}$$

where $v_1(r)$ is the d-dimensional volume of a single sphere of radius r given by[1]

$$v_1(r) = \frac{\pi^{d/2}}{\Gamma(1+d/2)} r^d, \tag{30}$$

and $\Gamma(x)$ is the gamma function.

It is clear that for the volume fraction Φ to remain bounded [i.e., for the sum (29) to converge], $\rho_k R_{M_k}^d$ must also remain bounded for all k, and thus we have that

$$\rho_k \propto \frac{1}{R_{M_k}^d}, \quad \forall\, k. \tag{31}$$

An important conclusion is that the number density ρ_k must diverge to infinity as R_{M_k} approaches zero. This in turn means that the specific surface s must also diverge, since $\rho_k R_{M_k}^{d-1}$ diverges as R_{M_k} approaches zero. Note that volume fraction ϕ_2 of the inclusion phase is given by

$$\phi_2 = \sum_{k=1}^{\infty} \rho_k v_1(R_{I_k}) = \frac{\pi^{d/2}}{\Gamma(1+d/2)} \sum_{k=1}^{\infty} \rho_k R_{I_k}^d. \tag{32}$$

It is convenient to introduce the following nth moment of R_I:

$$\langle R_I^n \rangle = \frac{1}{\rho} \sum_{k=1}^{\infty} \rho_k R_{I_k}^n, \tag{33}$$

where ρ is a characteristic density (e.g., the inverse of the volume of the largest composite sphere) and n is any integer $n \geqslant d$. Note that the inclusion volume fraction ϕ_2 can now be re-expressed as

$$\phi_2 = \rho \frac{\pi^{d/2}}{\Gamma(1+d/2)} \langle R_I^d \rangle. \tag{34}$$

B. Integral identities

Next, following Pham,[9,10] we evaluate some key integrals involving the Green's function of the Laplace operator for the coated-spheres microstructure. We will subsequently employ these integral identities to evaluate the void bounds for this model.

Let X_i $(i=1,2,\ldots,d)$ represent a Cartesian coordinate emanating from the center of the spherical representative volume. In the coated-spheres model, every spherical inclusion $\mathcal{S}_I \subset \mathcal{V}_2$ is coated by a concentric spherical shell $\mathcal{S}_M$ of the matrix phase $(\mathcal{S}_M \subset \mathcal{V}_1)$. Consider a composite sphere $\mathcal{S}_{IM} = \mathcal{S}_I \cup \mathcal{S}_M$ and construct a local Cartesian coordinate x_i emanating from the center of each inclusion $\mathcal{S}_I$ (or composite sphere $\mathcal{S}_{IM}$):

$$x_i = X_i + \text{constant}. \tag{35}$$

Since $\mathcal{V}$, $\mathcal{S}_I$, and $\mathcal{S}_{IM}$ are spherical regions, we have from the theory of harmonic potentials that for $d=3$

$$\int_{\mathcal{S}} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} = \begin{cases} -\dfrac{1}{6} x_i x_i + \text{constant}, & \mathbf{x} \in \mathcal{S} \\ \dfrac{R^3}{3\sqrt{x_i x_i}}, & \mathbf{x} \in \mathcal{V} \setminus \mathcal{S} \end{cases} \tag{36}$$

$$\int_{\mathcal{V}} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} = -\frac{1}{6} X_i X_i + \text{constant}, \quad \mathbf{x} \in \mathcal{V}, \tag{37}$$

and for $d=2$

$$\int_{\mathcal{S}} g(\mathbf{x}-\mathbf{y}) dy = \begin{cases} -\dfrac{1}{4} x_i x_i + \text{constant}, & x \in \mathcal{S} \\ -\dfrac{R^2}{2} \ln \sqrt{x_i x_i}, & \mathbf{x} \in \mathcal{V} \setminus \mathcal{S} \end{cases} \tag{38}$$

$$\int_{\mathcal{V}} g(\mathbf{x}-\mathbf{y}) dy = -\frac{1}{4} X_i X_i + \text{constant}, \quad \mathbf{x} \in \mathcal{V}, \tag{39}$$

where $\mathcal{S}$ represents $\mathcal{S}_I$ or $\mathcal{S}_{IM}$, R is the radius of $\mathcal{S}$, and repeating indices indicate a summation. Moreover, if we let $\mathcal{S}'_{IM}$ be any composite sphere apart from $\mathcal{S}_{IM}$ $(\mathcal{S}'_{IM} \cap \mathcal{S}_{IM} = \emptyset)$, then for points $x \in \mathcal{S}_{IM}$, we obtain the identities

$$\int_{\mathcal{S}'_I} g(\mathbf{x}-\mathbf{y}) dy = \phi_2 \int_{\mathcal{S}'_{IM}} g(\mathbf{x}-\mathbf{y}) dy, \tag{40}$$

$$\int_{\mathcal{S}'_M} g(\mathbf{x}-\mathbf{y}) dy = \phi_1 \int_{\mathcal{S}'_{IM}} g(\mathbf{x}-\mathbf{y}) dy, \tag{41}$$

where the inclusion $\mathcal{S}'_I \subset \mathcal{S}'_{IM}$ and the matrix $\mathcal{S}'_M \subset \mathcal{S}'_{IM}$. Using relations (36)–(41), we find what is called the "far-field interaction" via the harmonic potential for $\mathbf{x} \in \mathcal{S}_{IM}$, i.e., the contribution of the harmonic field at a point $\mathbf{x}$ inside $\mathcal{S}_{IM}$ from all of the inclusions outside of $\mathcal{S}_{IM}$:

$$\begin{aligned} \int_{\mathcal{V}_2 \setminus \mathcal{S}_I} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} &= \sum_{\mathcal{S}'_I \cap \mathcal{S}_I = \emptyset} \int_{\mathcal{S}'_I} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} \\ &= \phi_2 \int_{\mathcal{V} \setminus \mathcal{S}_{IM}} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} \\ &= \phi_2 \left(\int_{\mathcal{V}} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} - \int_{\mathcal{S}_{IM}} g(\mathbf{x}-\mathbf{y}) d\mathbf{y} \right) \\ &= \frac{\phi_2}{2d} (x_i x_i - X_i X_i) + \text{constant}. \end{aligned} \tag{42}$$

Similarly, we have

$$\int_{\mathcal{V}_1 \setminus \mathcal{S}_M} g(\mathbf{x},\mathbf{y}) d\mathbf{y} = \frac{\phi_1}{2d} (x_i x_i - X_i X_i) + \text{constant}. \tag{43}$$

IV. VOID LOWER BOUNDS ON THREE-DIMENSIONAL TRAPPING CONSTANT

A. Inclusions as the pore space

We first evaluate the void lower bound on γ for the three-dimensional coated-spheres model. To begin, we take the connected matrix phase $\mathcal{V}_1$ to be the traps and the disconnected inclusion phase $\mathcal{V}_2$ to be the pore space. Therefore, the porosity is given by $\phi_P=\phi_2$. Using the void trial field (13) for $v(\mathbf{x})$, we can obtain from Eq. (11) the lower bound on the trapping constant

$$\gamma \geqslant \left[\lim_{V\to\infty}\frac{1}{V}\int_{\mathcal{V}} \nabla v\cdot\nabla v \mathcal{I}^{(2)}(\mathbf{x})d\mathbf{x}\right]^{-1}, \tag{44}$$

where we have equated ensemble averages with volume averages via the ergodic hypothesis. We can explicitly calculate the void trial field $v(\mathbf{x})$ using identities (36), (37), and (42) for $x\in S_I$:

$$\begin{aligned}\phi_1 v(\mathbf{x}) &= \int_{V_2} g(\mathbf{x},\mathbf{y})d\mathbf{y} - \phi_2\int_V g(\mathbf{x},\mathbf{y})d\mathbf{y}\\ &= \int_{S_I} g(\mathbf{x},\mathbf{y})d\mathbf{y} + \int_{\mathcal{V}_2\setminus\mathcal{S}_{IM}} g(\mathbf{x},\mathbf{y})d\mathbf{y}\\ &\quad - \phi_2\int_V g(\mathbf{x},\mathbf{y})d\mathbf{y}\\ &= -\frac{1}{6}x_ix_i + \frac{\phi_2}{6}(x_ix_i - X_iX_i) + \frac{\phi_2}{6}X_iX_i + \text{constant}\\ &= -\frac{\phi_1}{6}x_ix_i + \text{constant}.\end{aligned} \tag{45}$$

Letting $r^2\equiv x_ix_i$, it follows that

$$\nabla v = -\frac{1}{3}x_i \quad\text{and}\quad \nabla v\cdot\nabla v = \frac{1}{9}r^2. \tag{46}$$

The lower bound (44) is readily calculated using the result immediately above:

$$\begin{aligned}\gamma^{-1} &\leqslant \lim_{V\to\infty}\frac{1}{V}\int_{\mathcal{V}_2}\nabla v\cdot\nabla v d\mathbf{x}\\ &= \lim_{V\to\infty}\frac{1}{V}\sum_{S_I\in\mathcal{V}_2}\int_{S_I}\frac{r^2}{9}d\mathbf{x}\\ &= \lim_{V\to\infty}\frac{1}{V}\frac{4\pi}{9}\sum_{S_I\in\mathcal{V}_2}\int_0^{R_I} r^4 dr\\ &= \lim_{V\to\infty}\frac{1}{V}\frac{4\pi}{45}\sum_{S_I\in\mathcal{V}_2} R_I^5\\ &= \frac{4\pi}{45}\sum_{k=1}^{\infty}\rho_k R_I^5 = \frac{\phi_2}{15}\frac{\langle R_I^5\rangle}{\langle R_I^3\rangle},\end{aligned}$$

where we have used the definitions (34) and (33). Based on our earlier discussion concerning restrictions on the size distribution, we see from the sum in the last line that the infinitesimally small spheres do not make any contribution to the trapping constant. Thus, using the fact that $\phi_2=\phi_P$, the void lower bound is exactly given by[32]

$$\gamma \geqslant \frac{15\langle R_I^3\rangle}{\phi_P\langle R_I^5\rangle}. \tag{47}$$

Interestingly, by comparing this result to the general expression for the void upper bound (16), which is given in terms of the two-point correlation function $S_2(r)$, we see that the square of the pore length scale ℓ_P for $d=3$ is exactly given by

$$\ell_P^2 = \int_0^\infty [\mathcal{S}_2(r)-\phi_P^2]r dr = \frac{\phi_P\phi_{\mathcal{S}}^2}{15}\frac{\langle R_I^5\rangle}{\langle R_I^3\rangle} \tag{48}$$

for the coated-spheres model.

Now we show that bound (47) coincides with the exact expression for the trapping constant for this particular coated-spheres model. Specifically, the exact solution of the boundary-value problem

$$\begin{aligned}&\nabla^2 u = -1, \quad \text{in} \quad \mathcal{S}_I,\\ &u = 0, \quad \text{on} \quad \partial\mathcal{S}_I,\end{aligned} \tag{49}$$

for diffusion inside a spherical inclusion $\mathcal{S}_I$ with $r^2=x_ix_i$ is given by[1]

$$u = \frac{1}{6}(R_I^2 - r^2), \quad 0 \leqslant r \leqslant R_I. \tag{50}$$

Therefore, using the definition (8), we find that γ, for *nonoverlapping* sphere models with a *general size distribution* (not just the coated-spheres model) is exactly given by

$$\begin{aligned}\gamma^{-1} = \langle u\rangle &= \lim_{V\to\infty}\frac{1}{V}\sum_{\mathcal{S}_I\in\mathcal{V}_2}\int_0^{R_I}\frac{1}{6}(R_I^2-r^2)4\pi r^2 dr\\ &= \lim_{V\to\infty}\frac{1}{V}\frac{4\pi}{45}\sum_{\mathcal{S}_I\in\mathcal{V}_2} R_I^5 = \frac{\phi_2}{15}\frac{\langle R_I^5\rangle}{\langle R_I^3\rangle},\end{aligned} \tag{51}$$

or

$$\gamma = \frac{15\langle R_I^3\rangle}{\phi_P\langle R_I^5\rangle}. \tag{52}$$

It is important to note that the void lower bound (47) coincides with the exact solution (52) for the coated-spheres model, and hence the bound is exactly realizable when the inclusions are taken to be the pore phase. This may immediately lead one to conclude that the void bound is optimal among all microstructures, but such a statement cannot be made unless one attaches special conditions. Recall that unlike the effective conductivity or effective elastic moduli, the trapping constant as well as the fluid permeability are length-scale dependent quantities. Thus, any statement about optimality must fix not only the porosity but the relevant length scales. The correct statement is the following: The void bound is optimal among all microstructures that share the same porosity ϕ_P and pore length scale ℓ_P defined by relation (17). Indeed, the bound is shown to be attained by the coated-spheres model. Observe that one can always adjust the pore length scale [Eq. (48)] of the coated-spheres model at some porosity ϕ_P to be equal to ℓ_P for any microstructure with the same porosity.

As noted above, relation (52) applies to diffusion within nonoverlapping spheres with a general size distribution. Accordingly, let us define another squared length scale $L_P^2 = \langle R_I^5 \rangle / \langle R_I^3 \rangle$ for such a general nonoverlapping sphere model. In what follows, superscripts g and c are appended to quantities associated with the general sphere model and coated-spheres model, respectively. The use of expressions (16), (47), and (52) reveals the following interrelations between these two models: At fixed ϕ_P, if $L_P^{(g)} = L_P^{(c)}$, then $\gamma^{(g)} = \gamma^{(c)}$ and $\ell_P^{(g)} \geq \ell_P^{(c)}$, and if $\ell_P^{(g)} = \ell_P^{(c)}$, then $\gamma^{(g)} \geq \gamma^{(c)}$ and $L_P^{(g)} \leq L_P^{(c)}$.

B. Matrix as the pore space

Here, we take the connected matrix phase $\mathcal{V}_1$ to be the pore space and the disconnected inclusion phase $\mathcal{V}_2$ to be the traps. Therefore, the porosity is given by $\phi_P = \phi_1$. Employing the void trial field (13) for $v(\mathbf{x})$, we can obtain from Eq. (11) the lower bound on the trapping constant

$$\gamma \geq \left[\lim_{V\to\infty} \frac{1}{V} \int_{\mathcal{V}} \nabla v \cdot \nabla v \mathcal{I}^{(1)}(\mathbf{x}) d\mathbf{x} \right]^{-1}. \quad (53)$$

We can evaluate the void trial field $v(\mathbf{x})$ using Eqs. (36), (37), and (43) for $\mathbf{x} \in \mathcal{S}_M$:

$$\phi_2 v(\mathbf{x}) = \int_{\mathcal{V}_1} g(\mathbf{x},\mathbf{y}) d\mathbf{y} - \phi_1 \int_{\mathcal{V}} g(\mathbf{x},\mathbf{y}) d\mathbf{y}$$
$$= -\frac{\phi_2}{6} x_i x_i - \frac{R_I^3}{3\sqrt{x_i x_i}} + \text{constant}. \quad (54)$$

It directly follows that

$$\nabla v = -\frac{1}{3} x_i - \frac{R_I^3 x_i}{3(x_k x_k)^{3/2} \phi_2}$$

$$\nabla v \cdot \nabla v = \frac{1}{9} x_i x_i + \frac{R_I^6}{9\phi_2^2 (x_i x_i)^2} + \frac{2R_I^3}{9\phi_2 (x_i x_i)^{1/2}}. \quad (55)$$

Now the void lower bound (53) can be calculated as

$$\gamma^{-1} \leq \lim_{\mathcal{V}\to\infty} \frac{1}{V} \int_{\mathcal{V}_1} \nabla v \cdot \nabla v d\mathbf{x}$$
$$= \frac{\langle R_I^5 \rangle}{\langle R_I^3 \rangle} \frac{1}{3\phi_2} \left(1 + \frac{1}{5}\phi_2^{1/3} - \phi_2 - \frac{1}{5}\phi_2^2\right). \quad (56)$$

Thus, identifying ϕ_2 with the volume fraction ϕ_S of the traps, we obtain the void lower bound for the model as

$$\frac{\gamma}{\gamma_s} \geq \left(1 + \frac{1}{5}\phi_S^{1/3} - \phi_S - \frac{1}{5}\phi_S^2\right)^{-1}, \quad (57)$$

where

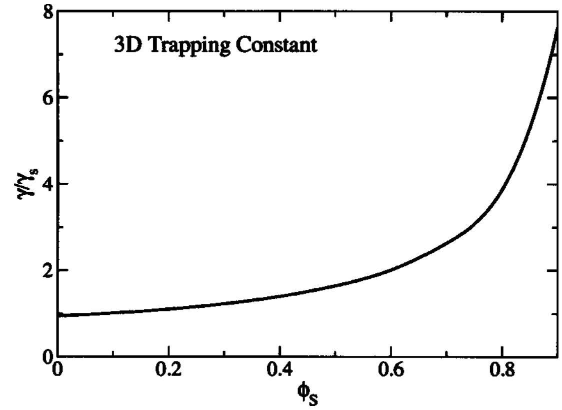

FIG. 2. Void lower bound (57) on the scaled trapping constant γ/γ_s vs solid phase volume fraction ϕ_S for diffusion in the matrix phase of the three-dimensional coated-spheres model.

$$\gamma_s = \frac{3\phi_S \langle R_I^3 \rangle}{\langle R_I^5 \rangle}. \quad (58)$$

We plot the void lower bound (57) over a range of ϕ_S in Fig. 2.

V. LOWER BOUNDS ON TWO-DIMENSIONAL TRAPPING CONSTANT

We can repeat the whole procedure of the previous section for the coated-cylinders model. The only difference is that one should use Eqs. (38) and (39) for the two-dimensional problems instead of Eqs. (36) and (37). The results are summarized below.

A. Inclusions as the pore space

For diffusion inside circular inclusions, we obtain the void lower bound as

$$\gamma \geq \frac{8\langle R_I^2 \rangle}{\phi_P \langle R_I^4 \rangle}, \quad (59)$$

which coincides with the exact result

$$\gamma = \frac{8\langle R_I^2 \rangle}{\phi_P \langle R_I^4 \rangle}. \quad (60)$$

Comparison of this result to the general relation for the void upper bound (16) yields the following exact expression for the square of the pore length scale ℓ_P for the coated-cylinders model:

$$\ell_P^2 = -\int_0^\infty [S_2(r) - \phi_P^2] r \ln r dr = \frac{\phi_P \phi_S^2}{8} \frac{\langle R_I^4 \rangle}{\langle R_I^2 \rangle}. \quad (61)$$

B. Matrix as the pore space

For diffusion exterior to the circular inclusions, we obtain the void lower bound as

$$\frac{\gamma}{\gamma_s} \geq \left(-\ln \phi_S - \frac{3}{2} + 2\phi_S - \frac{1}{2}\phi_S^2\right)^{-1} \quad (62)$$

where

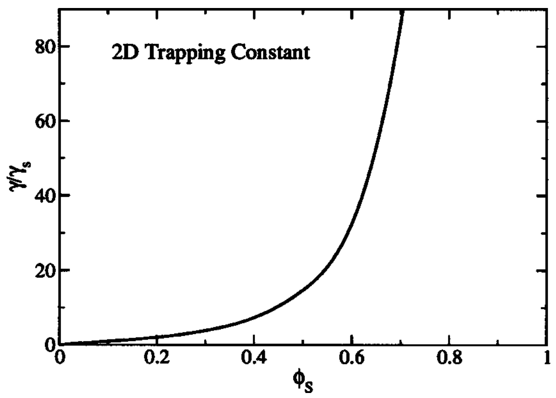

FIG. 3. Void lower bound (62) on the scaled trapping constant γ/γ_s vs solid phase volume fraction ϕ_S for diffusion in the matrix phase of the two-dimensional coated-cylinders model.

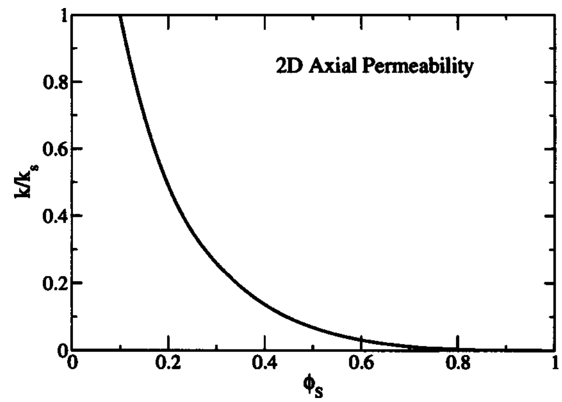

FIG. 4. Void upper bound (66) on the scaled permeability k/k_s vs solid phase volume fraction ϕ_S for axial flow in the matrix phase of the coated-cylinders model.

$$\gamma_s = \frac{4\langle R_I^2\rangle \phi_S}{\langle R_I^4\rangle}. \tag{63}$$

We plot the void lower bound (62) over a range of ϕ_S in Fig. 3.

VI. UPPER BOUNDS ON FLUID PERMEABILITY

A. Axial flow in the coated-cylinders model

Consider fluid flow along (inside or outside) bundles of parallel cylindrical circular tubes corresponding to the coated-cylinders model. The velocity field reduces to an axial compoenent only, and the Stokes equation reduces to a simple Poisson equation identical to that of the two-dimensional trapping problem [Eqs. (8)–(12)]. Hence, we have exactly the same solution for the axial component of velocity as for the concentration field in the trapping problem, leading to the exact result that $k=\gamma^{-1}$ (see Ref. 1). Exploiting this observation, we simply summarize the appropriate results below for k using the results of Sec. V.

1. Inclusions as the pore space

In particular, for axial flow inside the cylindrical tubes (Poiseuille flow) in the coated-cylinders model, the void upper bound on k is obtained from the lower bound (59) on γ and the identity $k=\gamma^{-1}$ (which applies only for this special geometry), i.e.,

$$k \leqslant \frac{\phi_P\langle R_I^4\rangle}{8\langle R_I^2\rangle}, \tag{64}$$

which coincides with the exact result[1] and thus is optimal. Thus, the exact expression for the square of the pore length scale ℓ_P for the coated-cylinders model in the *transverse* plane is given by Eq. (61).

A well-known empirical estimate for k is the Kozeny–Carman relation[1]

$$k = \frac{\phi_P^3}{cs^2}, \tag{65}$$

where c is an adjustable parameter and s is the specific surface defined by Eq. (4). However, for the coated-spheres or coated-cylinders models with the inclusions of all sizes down to infinitesimally small, we saw in Sec. III that s diverges to infinity and therefore the Kozeny–Carman relation incorrectly predicts a vanishing permeability. This serves to illustrate the well-established fact that the permeability cannot generally be represented by a simple length scale, such as the specific surface.[1,15,17] It should be pointed out that the permeabilities of real porous media with high tortuosities will lie well below the optimal void upper bound.

2. Matrix as the pore space

For flow exterior to the cylindrical tubes, we obtain the void upper bound as

$$\frac{k}{k_s} \leqslant -\ln \phi_S - \frac{3}{2} + 2\phi_S - \frac{1}{2}\phi_S^2 \tag{66}$$

where

$$k_s = \frac{\langle R_I^4\rangle}{4\phi_s\langle R_I^2\rangle}. \tag{67}$$

We plot the void upper bound (66) over a range of ϕ_S in Fig. 4.

B. Three-dimensional flow exterior to spherical obstacles

Here, we exploit the fact that the void upper bound (28) on k is trivially related to the void lower bound (16). Thus, we deduce the upper bound on k for flow exterior to spherical inclusions in the coated-spheres model from the corresponding bound (57) on the trapping constant:

$$k/k_s \leqslant 1 + \frac{1}{5}\phi_S^{1/3} - \phi_S - \frac{1}{5}\phi_S^2, \tag{68}$$

where

$$k_s = \frac{2\langle R_I^5\rangle}{9\phi_S\langle R_I^3\rangle}. \tag{69}$$

We plot the void upper bound (68) over a range of ϕ_S in Fig. 5.

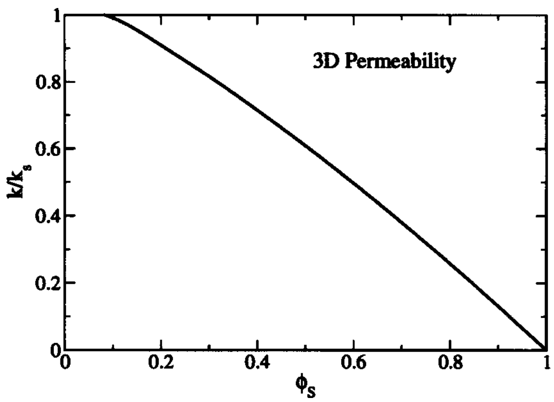

FIG. 5. Void upper bound (68) on the scaled permeability k/k_s vs solid phase volume fraction ϕ_S for flow in the matrix phase of the three-dimensional coated-spheres model.

VII. CONCLUSIONS

In contrast to bounds on the effective conductivity and elastic moduli of composite media, microstructures that exactly realize bounds on either the trapping constant or fluid permeability were heretofore unknown. The void lower bound (16) on the trapping constant γ and the void upper bound (28) on the fluid permeability k both generally depend on the pore length scale ℓ_P, defined by Eq. (17), which involves an integral over the two-point correlation function $S_2(r)$ that characterizes the porous medium. We have derived exact expressions for the void lower bounds on the trapping constant and void upper bounds on the fluid permeability for certain coated-spheres and coated-cylinders models of porous media. For diffusion inside the spherical $(d=3)$ and cylindrical inclusions $(d=2)$, the void lower bound on γ was shown to be exact. Similarly, for axial flow inside the cylinders of the coated-cylinders model, the void upper bound on k was demonstrated to be exact. In these instances, the void bounds are optimal among all microstructures that share the space porosity ϕ_P and pore length scale ℓ_P as the coated-spheres model. For cases of diffusion and flow exterior to the spheres and cylinders in the coated-inclusions model of porous media, exact results are not available, but we still obtained simple analytical expressions for the void bounds on γ and k.

In future studies, it will be of interest to investigate the optimal microstructures that correspond to the improved two-point "interfacial-surface" bounds on both γ and k.[1] In addition to depending on the two-point correlation function S_2, they also incorporate two-point surface correlation functions.

ACKNOWLEDGMENTS

The work was completed during the visit of one of the authors (D. C. P.) to the Materials Institute, Princeton University, as a Fulbright Senior Scholar. Another author (S. T.) was supported by the MRSEC Grant at Princeton University, NSF DMR - 0213706, and by the Air Force Office of Scientific Research under Grant No. F49620-03-1-0406.

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[31] The similarity between the void upper bound on k and the void lower bound on γ indicates a deeper relationship between these two properties, despite the fact that their corresponding governing field equations are different both in functional form and tensorial order. Indeed, it was shown in Ref. 12 (see also Ref. 1) that the inverse of the *isotropic* trapping constant tensor bounds the fluid permeability tensor from above for general statistically homogeneous porous media.
[32] Alternatively to Eq. (33), if we define the volume-weighted average on V for a function $f(R_I)$ as $\langle f(R_I)\rangle_V=(1/\phi_2)\Sigma_{S_I\in V_2}v_1(R_I)f(R_I)$, where $v_1(r)$ is given by Eq. (30), then $\langle R_I^{d+2}\rangle/\langle R_I^d\rangle$ in Eq. (47) and subsequent expressions for γ, k, and ℓ_P would be replaced by $\langle R_I^2\rangle_V$.